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(54) PREPARATION OF POLYMERIC ANTIOXIDANTS

(71) We, CIBA-GEIGY AG, a Swiss Company of CH—4002, Basle, Switzerland, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

The present invention is concerned with a novel process for the production of compounds which are useful as antioxidants for organic materials, particularly as antioxidants for such materials as polypropylene, polyethylene, polystyrene, polyvinyl chloride, nylon and other polyamides, polyesters, cellulosics, polyacetals, polyurethanes, petroleum and wood resins, mineral oils, animal and vegetable fats, waxes, rubbers such as styrene-butadiene rubber (SBR), acrylonitrile-butadiene-styrene rubber (ABS), olefin-copolymers such as ethylene-vinyl acetate copolymers, polycarbonates, polyacrylonitrile, poly(4-methyl pentene-1) and polyoxy-methylenes.

The prevention of oxidation of various organic materials is obviously of primary industrial concern and therefore antioxidants are used in or added to a wide variety of commercial products such as synthetic polymers of the type indicated *supra*, oils and plastics, which are normally subject to oxidative deterioration.

The mechanism of the action of a hindered phenol compound as an antioxidant has not been definitely established but it is believed that the hindered phenol acts as a chain-stopper for the free radical chain mechanism of oxidation either by donation of hydrogen or donation of an electron to a free radical involved in the oxidation process or the combination of a free radical with the aromatic ring of the antioxidant either by direct addition or by π complex formation.

Since it is generally believed that free radicals, necessary for the polymerization of vinyl- and related monomers, are trapped by antioxidants such as hindered phenols, polymerizations of vinyl monomers carrying a phenolic group or a hindered phenolic group were carried out by a series of steps which included esterification of the phenol group, free radical polymerization of the vinyl group followed by hydrolysis of the ester group to obtain the desired polymeric antioxidant. This procedure is illustrated by S. N. Ushakov et al., USSR Patent 149,888 as follows:

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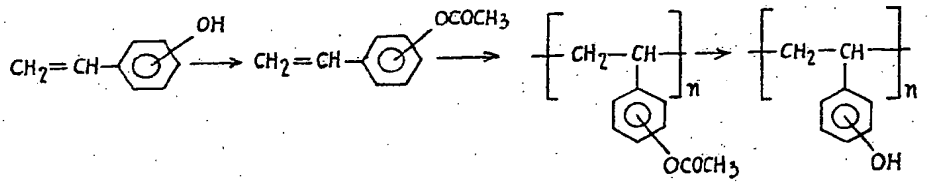
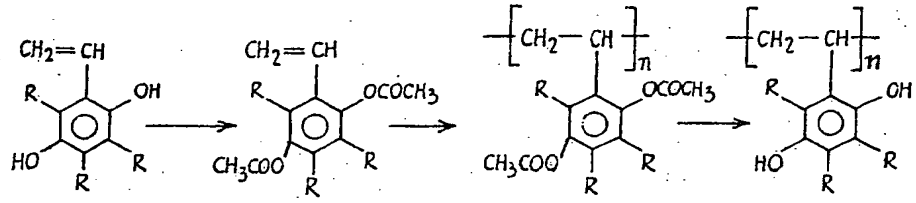


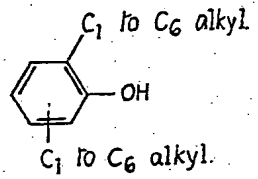
and by G. Manecke+G. Bourweig, Makromolekulare Chemie, 99 (1966) 175—185 as follows:



(R=C_1—C_3 alkyl).

It has now been found that monomers containing hindered phenolic groups can be directly polymerized by free alkyl- or aryl- radicals to produce the desired polymeric antioxidants of the present invention.

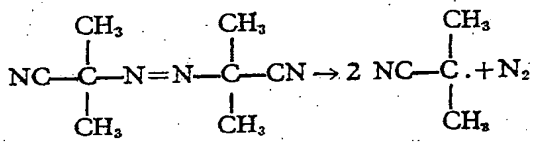
According to the present invention there is provided a process for the preparation of a polymeric antioxidant compound which comprises subjecting to polymerising conditions (a) a monomeric ester, thioester, amide or imide of an α,β-ethylenically unsaturated carboxylic acid containing in the moiety attached to the α,β-ethylenically unsaturated carboxylic acyl moiety a phenol group of the formula:



and (b) a free radical initiator which is an azo derivative, or an aliphatic or cycloaliphatic acyl peroxide.

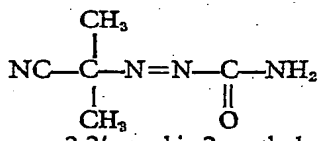
Thus, in the present invention, a single step process is utilised in the preparation of the desired polymeric antioxidants thereby avoiding the multi-step procedures of the prior art set out above.

An essential reactant in the preparation of the polymeric antioxidants of the present invention is an initiator which can react with the antioxidant monomer to obtain directly, i.e., in one step, the desired polymeric antioxidants. Included among the initiators are azo-nitriles and other azo-derivatives which dissociate into aliphatic- or aryl-free radicals at temperatures convenient for polymerisation reaction. The best known example of an azo-nitrile is 2,2′-azobisisobutyronitrile and the dissociation providing the required cyano-alkyl free radical is shown as follows:



Other azo-nitriles and azo-derivatives which can be used to react with the aforesaid antioxidant monomers to prepare the desired products of the invention are described in J. Brandrup and E. H. Immergut, Polymer Handbook (John Wiley and Sons) 1965 pages II—3 to II—14 and include, for example

2-(2-methyl propionitrile)-azo-formamide



2,2'-azo-bis-2-methylpropionitrile
1,1'-azo-bis-1-cyclobutanenitrile
2,2'-azo-bis-2-methylbutyronitrile
4,4'-azo-bis-4-cyanopentanoic acid
1,1'-azo-bis-1-cyclopentanenitrile
2,2'-azo-bis-2-methylvaleronitrile
2,2'-azo-bis-2-cyclobutylpropionitrile
1,1'-azo-bis-1-cyclohexane nitrile
2,2'-azo-bis-2,4-dimethylvaleronitrile
2,2'-azo-bis-2,4,4-trimethylvaleronitrile
2,2'-azo-bis-2-benzylpropionitrile
1,1'-azo-bis-1-cyclodecane nitrile
azo-bis-(1-carbomethoxy-3-methylpropane)
phenyl-azo-diphenylmethane
phenyl-azo-triphenylmethane
azo-bis-diphenylmethane
3-tolyl-azo-triphenylmethane

As indicated above certain acyl peroxide-initiators are similarly useful in preparing the desired polymeric antioxidant products of the present invention, the operative or useful peroxide-initiators being those capable of decomposing instantly into aliphatic or cycloaliphatic free radical. The aliphatic or cycloaliphatic free radical is obtained either by instantaneous decomposition or by a rearrangement reaction of the primary decomposition products of the peroxide compound. Of the stated peroxides, the aliphatic acyl peroxides are most useful and one preferred aliphatic acyl peroxide is acetyl peroxide. The decomposition of this compound into alkyl free radicals can be set out as follows:

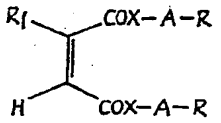
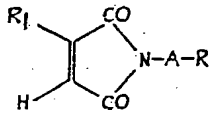
$$CH_3COO—OCOCH_3 \xrightarrow{I} 2CH_3COO\cdot \xrightarrow{II} 2CH_3\cdot + 2CO_2$$

Reaction II follows Reaction I instantaneously. In the presence of iodine, only CH_3I is isolated; proof of the instantaneous formation of the methyl radical. In addition to acetyl peroxide, and also lauroyl peroxide and decanoyl peroxide, the preferred peroxides, other aliphatic and cycloaliphatic acyl peroxides containing up to 18 carbon atoms in each acyl group are also useful as initiators for the polymerization of antioxidant monomers. Such peroxide compounds include propionyl peroxide, butyryl peroxide, isobutyryl peroxide, cyclobutaneacetyl peroxide, heptanoyl peroxide, caprylyl peroxide, cyclohexane acetyl peroxide, nonanoyl peroxide, myristoyl peroxide and stearyl peroxide.

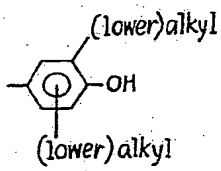
Aromatic acyl peroxides such as benzoyl peroxide and 2,4-dichlorobenzoyl peroxide were also investigated. However, no polymerization occurred due to the fact that the intermediate benzoyloxy radicals do not decompose instantaneously into phenyl radicals but instead abstract hydrogen from the hydroxy group of the antioxidant.

Dialkyl peroxides and particularly di-tertiary-butyl peroxide were also investigated as possible polymerization initiators. However, in the presence of antioxidant monomers, is was found that t-butyl alcohol was the main decomposition product indicating that the alkoxy radical abstracts hydrogen rather than adds to the double bond of the antioxidant monomer. Peresters were also investigated but it was found that these compounds oxidize and do not polymerize antioxidant monomers. Another group of compounds which was studied for possible use as polymerization initiators were the hydroperoxides and a typical example was t-butyl hydroperoxide. It was found however, that this last mentioned compound, when it was reacted with an antioxidant monomer, did not produce polymerization since no alkyl radicals were simultaneously formed during the decomposition. It is believed that the other hydroperoxides behave similarly.

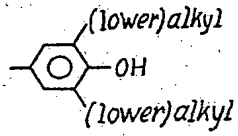
Some of the monomers used to produce the polymeric antioxidants of the present invention are included within the following classes of compounds:

Monomer	Structure
esters, thioesters and amides of acrylic and methacrylic acid	$CH_2=C(R_1)—COX—A—R$
esters, thioesters and amides of maleic acid (R_1=H, cis) fumaric acid (R_1=H, trans) citraconic acid (R_1=CH_3, cis) mesaconic acid (R_1=CH_3, trans)	
imides of maleic acid and citraconic acid	
esters, thioesters and amides of itaconic acid	$CH_2=C(—CH_2—COX—A—R)—COX—A—R$
esters, thioesters and amides of crotonic and cinnamic acid	$CH_3—CH=CH—COX—A—R$ $C_6H_5—CH=CH—COX—A—R$

wherein R is



and preferably



R_1 is H or CH_3

—X— is —O—, —S—, —NH, —N(lower)alkyl- and

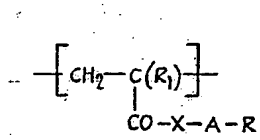
—A— is

$—C_nH_{2n}—$
$—C_mH_{2m}—COX—C_nH_{2n}—$,
$—(C_mH_{2m}X)_oCO—C_nH_{2n}—$, and preferably $—CH_2CH_2XCOCH_2CH_2—$
$—C_mH_{2m}—CO—C_nH_{2n}—$
$—C_mH_{2m}—O—C_nH_{2n}$
$—C_mH_{2m}—NH—COO—C_nH_{2n}—$

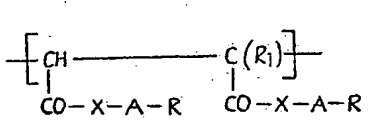
n is 0 to 6, and $C_n H_{2n}$ is straight or branched
m is 1 to 6, and $C_m H_{2m}$ is straight or branched
o is 1 to 3

"Lower alkyl" as used herein means alkyl groups containing up to and including 6 carbon atoms and illustratively includes methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl and hexyl.

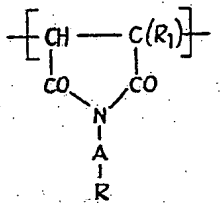
The corresponding polymers of the above monomers are those having repeating units of



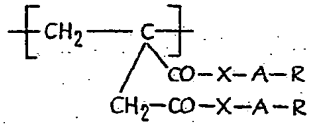
(esters, thioesters and amides of acrylic and methacrylic acid)



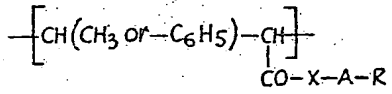
(esters, thioesters and amides of maleic, fumaric, citraconic and mesaconic acid)



(imides of maleic and citraconic acid)



(esters, thioesters and amides of itaconic acid)

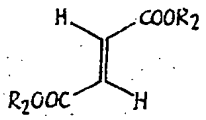
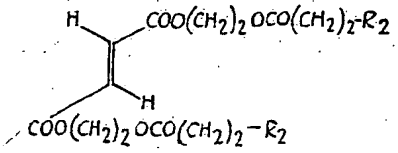


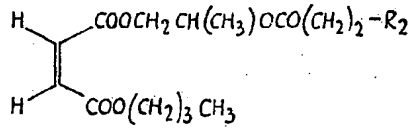
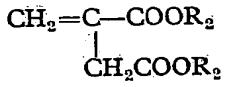
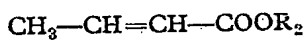
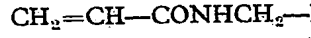
(esters, thioesters and amides of crotonic and cinnamic acid)

wherein R, R_1, —X— and —A— have the same meaning as given above.

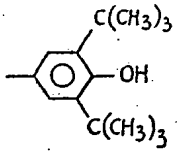
Of the different classes of monomers set out above, the preferred group of monomers are the esters, thioesters and amides of acrylic, methacrylic, fumaric and itaconic acids.

In the aforementioned groups of antioxidant monomers, illustrative specific monomers used in preparing the polymeric antioxidants of the present invention are as follows:

Compound	Structure
3,5-di-tert-butyl-4-hydroxyphenyl acrylate	$CH_2=CH—COO—R_2$
3,5-di-tert-butyl-4-hydroxyphenyl methacrylate	$CH_2=C(CH_3)—COO—R_2$
3-(3,5-di-tert-butyl-4-hydroxyphenyl)propyl methacrylate	$CH_2=C(CH_3)—COO(CH_2)_3—R_2$
2-(3,5-di-tert-butyl-4-hydroxybenzoyloxy)ethyl methacrylate	$CH_2=C(CH_3)—COO(CH_2)_2OCO—R_2$
2-(3,5-di-tert-butyl-4-hydroxyphenylacetoxy)ethyl methacrylate	$CH_2=C(CH_3)—COO(CH_2)_2OCOCH_2—R_2$
2-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy]-ethyl methacrylate	$CH_2=C(CH_3)—COO(CH_2)_2OCO(CH_2)_2—R_2$
2-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy]-ethyl acrylate	$CH_2=CH—COO(CH_2)_2OCO(CH_2)_2—R_2$
2-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy]-propyl acrylate	$CH_2=CH—COO—CH_2CH(CH_3)OCO(CH_2)_2—R_2$
2-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy]-propyl methacrylate	$CH_2=C(CH_3)—COOCH_2CH(CH_3)OCO(CH_2)_2—R_2$
bis(3,5-di-tert-butyl-4-hydroxyphenyl) fumarate	
bis{2-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy]-ethyl}fumarate	

Compound	Structure
n-butyl 2-[3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy]-propyl maleate	
bis(3,5-di-tert-butyl-4-hydroxyphenyl) itaconate	
3,5-di-tert-butyl-4-hydroxyphenyl crotonate	
3,5-di-tert-butyl-4-hydroxyphenyl cinnamate	
N-(3,5-di-tert-butyl-4-hydroxybenzyl)-acrylamide ①	

① Disclosed in French Patent 1457152

wherein R_2 is 

Of the antioxidant monomers set out above, the preferred monomers are the acrylates and methacrylates.

The three general procedures for preparing the antioxidant monomers used in producing the polymeric antioxidants of the present invention are as follows:

Procedure A—To one mole of the alcohol or phenol (as set out in Table I below) dissolved in five times the amount of pyridine is added, accompanied by vigorous stirring, at 5°—10°C, one mole of the acid chloride (as set out in Table I) as a 33% by weight solution while maintaining the temperature below 25°C. After the addition is completed, that is, within about 15—25 minutes, the reaction mixture is stirred at room temperature for 1 to 2 hours. The precipitated hydrochloride is filtered, the solvent and excess pyridine is evaporated and the residue, after addition of ether, is washed with 2 N hydrochloric acid and then with water. The separated ether layer is dried over sodium sulfate, filtered and evaporated. The residue is then purified either by high vacuum distillation or recrystallization, as indicated in Table I. Yields are very high that is, between about 70 and 95%.

Procedure B—Equimolar amounts of acid chloride and alcohol or phenol (as set out in Table I below) are refluxed in twice the amount of benzene or toluene for a period between 12 and 36 hours (refluxed is stopped if conversion is high enough as determined by vapor phase chromatography or thin layer chromatography). The reaction mixture is then washed with 2 N potassium bicarbonate solution and then with water. The organic layer is dried over sodium sulfate and after evaporation of the solvent, the crude product is purified either by high vacuum distillation or by recrystallization as indicated in Table I below. Yields are in the range of 65 to 85%.

Procedure C—One mole of the phenol is dissolved in 3 to 5 moles of the acid chloride and refluxed for 1 to 3 hours, (refluxing is stopped if conversion is complete as determined by vapor phase chromatography or thin layer chromatography). The excess acid chloride is then removed by distillation and after washing the powdery residue with hexane or heptane to remove the last traces of the acid chloride, the residue is purified by recrystallization, as indicated in Table I. The yields are excellent varying between 80 and 95%.

The last procedure set out above is the preferred one in view of the short reaction time, very high yields and simple work-up procedure if the excess acid chloride can be easily removed as in the case of acrylyl chloride, methacrylyl chloride, crotonyl chloride, cinnamoyl chloride, etc. If the boiling point of the acid chloride is too high, the above-described Procedure C is carried out using solvent such as benzene, toluene, etc.

The starting materials used in preparing the antioxidant monomers as well as the properties of said monomers are set out in Table I below. In the last column of the chart, there is set out the method of synthesis used and reference should be made to the procedures which are set out above.

TABLE I

Monomer	Appearance	M.P. (°C.) (Crystallized from)	B.P. (°C.) (mm Hg)		Elemental Analysis Calc.	Elemental Analysis Found	Starting Material: Acid Chloride	Starting Material: Alcohol	Method of Synthesis
3,5-di-tert-butyl-4-hydroxyphenyl acrylate	White crystals	102.5°—103.5° (heptane)	—	C H	73.88 8.75	73.95 8.93	Acrylyl chloride	2,6-di-tert-butylhydroquinone	(A)
3,5-di-tert-butyl-4-hydroxyphenyl methacrylate	White crystals	137°—137.5° (heptane)	—	C H	74.44 9.03	74.15 8.73	Methacrylyl chloride	2,6-di-tert-butylhydroquinone	(A)
3-(3,5-di-tert-butyl-4-hydroxyphenyl)propyl methacrylate	Viscous oil solidifies after distillation	~60°	157°/0.1 mm	C H	75.86 9.70	75.63 9.83	Methacrylyl chloride	3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-propanol	(A)
2-(3,5-di-tert-butyl-4-hydroxybenzoyloxy)ethyl methacrylate	White crystals	71.5—72° (heptane)	—	C H	69.58 8.34	69.74 8.34	3,5-di-tert-butyl-4-hydroxybenzoyl chloride	2-hydroxyethyl methacrylate	(A)
2-(3,5-di-tert-butyl-4-hydroxyphenylacetoxy)ethyl methacrylate	White crystals	54.5—56° (heptane)	174°/0.2 mm	C H	70.18 8.57	70.16 8.41	3,5-di-tert-butyl-4-hydroxyphenylacetyl chloride	2-hydroxyethyl methacrylate	(A)
2-[3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionyloxy]ethyl methacrylate	Colorless viscous oil	—	196°/0.1 mm	C H	70.74 8.78	70.54 8.66	3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionyl chloride	2-hydroxyethyl methacrylate	(A)
2-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy]ethyl acrylate	Colorless viscous oil	—	181°/0.1	C H	70.18 8.57	69.89 8.60	3-(3,5-di-tert-butyl-4-hydroxy-phenyl)-propionyl chloride	2-hydroxyethyl acrylate	(A)
2-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy]-propyl acrylate	Colorless viscous oil	—	181°/0.2 mm	C H	70.74 8.78	70.60 8.57	3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyl chloride	2-hydroxypropyl acrylate	(A)

TABLE I (continued)

Monomer	Appearance	M.P. (°C.) Chrystallized from	B.P. (°C.) (mm Hg)	Elemental Analysis	Calc.	Found	Starting Material: Acid Chloride	Starting Material: Alcohol	Method of Synthesis
2-[3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionyloxy]propyl methacrylate	Colorless Viscous oil	—	178°/0.05 mm	C H	71.25 8.97	71.26 8.89	3-(3,5-di-tert-butyl-4-hydroxy-phenyl) propionyl chloride	2-hydroxy-propyl methacrylate	(A)
bis(3,5-di-tert-butyl-4-hydroxy-phenyl) fumarate	Yellow crystals	205—205.50 (heptane-benzene)	—	C H	73.25 8.45	73.49 8.40	fumaryl chloride	2,6-di-tert-butyl-hydroquinone[2]	(B)
bis{2-[3-(3,5-di-tert-butyl-4-hydroxy-phenyl)propionyloxy]-ethyl} fumarate	White crystals	99.5—100.5 (hexane)	—	C H	69.58 8.34	69.52 8.50	fumaryl chloride	2-hydroxyethyl-3-(3,5-di-tert-butyl-4-hydroxy-phenyl)-propionate[2]	(B)
n-butyl-2-[3-(3,5-di-tert-butyl-4-hydroxy-phenyl)propionyloxy]-propyl maleate	Colorless viscous oil	—	228—230° 0.6 mm	C H	68.54 8.63	68.74 8.33	3-(3,5-di-tert-butyl-4-hydroxy-phenyl)pro-pionyl chloride	hydroxy-propyl-n-butyl maleate	(B)
bis(3,5-di-tert-butyl-4-hydroxy-phenyl) itaconate	White crystals	145—146° (heptane)	—	C H	73.57 8.61	73.59 8.61	itaconyl chloride	2,6-di-tert-butylhydroquinone	(B)
3,5-di-tert-butyl-4-hydroxyphenyl crotonate	White crystals	80.5—81.5° (heptane)	—	C H	74.44 9.03	74.89 9.23	crotonyl chloride	2,6-di-tert-butylhydroquinone	
3,5-di-tert-butyl-4-hydroxyphenyl cinnamate	White crystals	125—126° (heptane)	—	C H	78.37 8.01	(not analysed)	cinnamoyl chloride	2,6-di-tert-butylhydroquinone	(C)
N-(3,5-di-tert-butyl-4-hydroxybenzyl)-acrylamide	White crystals	114—116° (Ethanol water)		French Patent No. 1,457,152					

[2] This alcohol is prepared by the following procedure:

The monoester of 3,5-di-tert-butyl-4-hydroxyphenylpropionyl chloride and ethylene glycol was prepared using Procedure A described above and a 20 molar excess of ethylene glycol. The product was purified (using the work-up procedure described in Method A supra) by column chromatography using Alox I neutral and was further purified by recrystallization from heptane. The product was obtained in the form of white crystals melting between 87.5° and 88.5°C.

Elemental Analysis:	Calculated:	C,	70.77%,	H	9.38%
	Found:		70.81%		9.40%

It has been found that where the polymer requiring protection against oxidative degradation is a solid material, for example, a polypropylene, polyethylene, nylon, polyacetal, polyurethane, styrene-butadiene rubber or acrylonitrile-butadiene-styrene rubber, the polymeric antioxidant should have a relatively low molecular weight, i.e., it should be an oligomeric substance, i.e. a polymer having a molecular weight between 400 and 6000. The most useful and the highest antioxidant activities are obtained by the used of oligomers having a molecular weight between 500 and 1500. Polymeric antioxidants having a higher degree of polymerization are not compatible with high molecular weight polymers and are therefore less effective with substances of this type.

It has also been found that where the polymeric material requiring protection against oxidative degradation is not a solid material but is a liquid or a semi-liquid, for example, an oil or a wax, the polymeric antioxidants may have a higher molecular weight, i.e. a molecular weight in excess of about 6000. With a higher degree of polymerization, there are sometimes secondary goals or advantages that may be achieved. In oils, for instance, high molecular weight polymeric antioxidants act additionally as thickening agents and viscosity index improvers.

As indicated supra, polymeric antioxidants are useful as additives to different polymeric systems. However, it is also possible to copolymerize minor amounts of an antioxidant monomer in amounts varying between 0.05 and 5% and preferably from 0.1 to 2% by weight based on total monomers, with other monomers which form polymers requiring protection against oxidative degradation. In such a case, the antioxidant-monomer moiety forms an integrated part of the polymer system. Small amounts of antioxidant monomers may therefore be copolymerized with butadiene-styrene, acrylonitrile-butadiene-styrene, ethylene and other monomers which form polymers that require protection against oxidative degradation. Thus, depending upon the end use, antioxidant monomer moieties may be a part of an oligomeric or a high molecular weight polymer system.

If the antioxidant monomer moiety is not a copolymerized part of the polymer requiring protection against oxidative degradation, the antioxidant polymers can be incorporated into polymers using conventional procedures. For example, the polymeric antioxidants of the present invention are incorporated into the material to be stabilized by any suitable means such as by milling the antioxidant on hot or cold mill rolls, by mixing it in by the use of a Banbury mixer or other well-known devices of this nature or the antioxidant may be mixed with a polyolefin material in the form of molding powder and incorporated during extrusion or prior to extrusion or during injection molding. The antioxidant may even be incorporated into a solution of a polyolefin

material which solution may then be employed for the formation of films, for wet or dry spinning of fibers, monofilaments and the like.

It should be mentioned that the polymers contemplated by the present invention include homopolymers of the novel antioxidant monomers and copolymers thereof with other ethylenically unsaturated monomers. Polymerization of the monomers may be carried out in bulk, solution, suspension or emulsion according to techniques well known to those skilled in the art. The preferred polymerization technique is the solution polymerization procedure using solvents as benzene, toluene, xylene and other aromatic solvents or chlorinated solvents such as chloroform and tetrachloroethylene, and initiators as described supra in quantities varying between 0.01% and 2% based upon the weight of the monomers. Polymerization temperatures are dependent upon the initiator used and are usually between 40° and 100°C.

It was also found that, in conducting the polymerization, conventional solvents could be advantageously replaced by the use of either distearylthiodipropionate or dilaurylthiodipropionate. These compounds are referred to as "synergists" since they increase the activity or effect of the polymeric antioxidants of the present invention. The aforesaid synergists are used in weight ratios of approximately three parts synergist to one part antioxidant. Further, by using either distearylthiodipropionate or dialaurylthiodipropionate as solvents in the polymerizations of antioxidant monomers, two important advantages are obtained: (1) the solvent stripping operation after the polymerization is eliminated and (2) the antioxidant polymer-synergist mixture solidifies at room temperature after the polymerization to a white mass which can be easily pulverized. Such powders are preferred as additives as compared with highly viscous or solid polymers.

The following description and Tables illustrate the procedures used in the preparation of polymeric antioxidants of the present invention and also illustrate the various tests conducted with respect to such polymeric antioxidants. These are not to be considered as limiting but only as illustrative of the present invention. All percentages given in the Tables are by weight.

The homopolymerization of representative members of antioxidant monomers, i.e., 2-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy]ethyl methacrylate and 3,5-di-tert-butyl-4-hydroxyphenyl methacrylate with different initiators to produce the corresponding polymeric antioxidants is set out in Table II below. The polymerization is effected, for example, by dissolving 4×10^{-3} moles of the monomer and 8×10^{-5} moles of the initiator in three times the amount of benzene. The polymerization is conducted under nitrogen and using the temperature and time set out in Table II. Under these conditions, the polymerization is interrupted after 1.5 half life-times of every initiator.

TABLE II

Initators (0.02 moles/mole Monomer)	Polym. Temp. (°C.)	Polym. Time (Hrs)	Yield of Homo Polymer [3]	Yield of Homo-Polymer [4]
2-(2-methyl propionitrile azoformamide	100	23	88.8%	75.6%
2,2'-azo-bis-isobutyronitrile	65	19.5	86.7%	84.5%
1,1-azo-bis-1-cyclohexane-carbonitrile	85	19.5	91.9%	84.8%
acetyl peroxide	67.5	18	70.8%	69.5%
decanoyl peroxide	60	18	70.5%	75.4%
lauroyl peroxide	60	18	88.9%	84.5%
2,4-dichlorobenzoyl peroxide	52	19.5	None	None
benzoyl peroxide	70	19.5	None	None
tert-butyl peroxide	125	19.5	None	None
cumyl peroxide	115	18	None	None
tert-butyl hydroperoxide	160	43.5	None	None
cumene hydroperoxide	155	19.5	None	None
tert-butyl peracetate	100	19.5	None	None
tert-butyl perpivalate	52	19.5	None	None
tert-butyl perbenzoate	105	19.5	None	None

[3] 2-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy]ethyl methacrylate polymer

[4] 3,5-di-tert-butyl-4-hydroxyphenyl methacrylate polymer

The results set out above indicate that only by use of the operable indicated initiator compounds can the polymerization be effected.

The following table illustrates the homopolymerization of the preferred acrylate and methacrylate antioxidant monomers. In the indicated polymerizations, ten parts of the monomer, 20 parts of chloroform and 0.2 part of 2,2'-azo-bis-isobutyronitrile, all by weight, are used, under nitrogen, and the mixture is polymerized for 16 hours at 80°C. The symbol Tg refers to the second order transition temperature and the symbol Tm refers to the melting temperature.

TABLE III

Monomer	Yield % By Weight	Differential Thermal Anal. Tg (°C.)	Tm (°C.)
3,5-di-tert-butyl-4-hydroxyphenyl acrylate	79	Not distinct	+148
3,5-di-tert-butyl-4-hydroxyphenyl methacrylate	76.3	„	+178
3-(3,5-di-tert-butyl-4-hydroxyphenyl)propyl methacrylate	65.8	+55 to 60	Not distinct
2-(3,5-di-tert-butyl-4-hydroxybenzoyloxy)ethyl methacrylate	82	+111	+125
2-(3,5-di-tert-butyl-4-hydroxyphenylacetoxy)-ethyl methacrylate	92.5	+58 to 63	+95
2-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy]-ethyl methacrylate	81.2	+29 to 30	+100
2-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy]-ethyl acrylate	97.4	+24	+70 to 80
2-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy]-propyl acrylate	74.2	+7	+42
2-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy]-propyl methacrylate	75.8	+42	+57 to 58
N-(3,5-di-tert-butyl-4-hydroxybenzyl)-acrylamide	79.45	+138	+172

In all instances the polymeric antioxidants are obtained in the form of a white powder. Using benzoyl peroxide as an initiator, no polymerization occurs.

The following Table illustrates the preparation of homopolymers, both oligomers and high molecular weight polymers, of 3,5-di-tert-butyl-4-hydroxyphenyl methacrylate. In preparing these homopolymers, one mole of the aforesaid monomer (and the octyl mercaptan in the indicated ratios) and 0.01 mole of 2,2'-azo-bis-isobutyronitrile are dissolved in twice the volume of chloroform. The polymerization is conducted under nitrogen, at a temperature of 80°C for a period of 16 hours. The resulting polymer product is not fractionated but is obtained by evaporation of the solvent. The molecular weight is determined by osmometry or vapor pressure osmometry.

TABLE IV

Appearance of Polymer	Moles Mercaptan / Moles Monomer	Aver. Mol. Weight Calculated	Aver. Mol. Weight Found	Tm(°C.)
White brittle powder	1/2	727	935	+55
"	1/3	1017	1176	+66
"	1/4	1307	1336	+72
"	1/6	1888	1888	+83
"	None	—	81,400	+178

It should be mentioned that in the preparation of oligomers that is, low molecular weight antioxidants, the polymerization is desirably carried out in the presence of chain transfer agents, for example, mercaptans. Illustrative of such chain transfer agents are alkyl mercaptans such as n-octyl, n-dodecyl and n-hexadecyl mercaptans.

Comonomers are important in the syntheses of oligomeric and polymeric antioxidants in that they can modify the physical properties of the polymeric antioxidant that is, the solubility characteristics as well as the solid state properties of the polymeric antioxidant can be influenced and in addition, the use of expensive antioxidant monomers can be modified by or set off by the use of cheap comonomers.

The copolymerization behavior of antioxidant monomers is predictable from their monomer class that is, an antioxidant monomer of the acrylate or methacrylate type behaves in a manner similar to an alkyl acrylate or alkyl methacrylate. Likewise, an antioxidant monomer of the fumarate type behaves in a manner similar to that of an alkyl fumarate in a copolymerization. Comonomers that can be used in copolymerization with acrylates, methacrylates, styrenes, fumarates and itaconates, are well known to those skilled in the art and are described, for example, in detail, in C.E. Schildknecht, "VINYL AND RELATED POLYMERS" published by John Wiley & Sons, New York, 1952.

Using acrylate and methacrylate antioxidant monomers, the preferred comonomers are alkyl (1 to 24 carbon atoms) acrylates and methacrylates, styrenes, vinyl esters, butadiene and isoprene including chlorinated or fluorinated derivatives thereof. Using fumarate and itaconate and related diester antioxidant monomers, the preferred comonomers are vinyl ethers, vinyl esters, alpha-olefins, styrenes and N-vinyl monomers.

The following Table illustrates the preparation of alternating copolymers of a representative sample of comonomers with antioxidant fumarates or maleates. The polymerization is conducted using equimolar amounts of the monomers which are dissolved in equal amounts of chloroform and polymerized using 2% by weight of the monomers of 2,2'-azo-bis-isobutyronitrile. The polymerization is conducted at a temperature of 80°C for 16 hours, under nitrogen.

TABLE V

Anti-oxidant Monomer	Co-Monomer	Appearance	Differential Thermal Analysis Tg(°C.)	Tm(°C.)		Elemental Analysis Calc. [5]	Found
bis{2-[3-(3,5-di-tert-butyl-4-hydroxy-phenyl)propionyloxy]ethyl} fumarate	methyl vinyl ether	yellowish powder	+30 to 37	+50	C H	69.02 8.50	69.14 8.67
n-butyl-2-[3-(3,5-di-tert-butyl-4-hydroxy-phenyl)propionyloxy]propyl maleate	vinyl acetate	white tacky polymer	—	—	C H	66.64 8.82	66.21 8.63
" "	methyl vinyl ether	white brittle polymer	+29	+69	C H	67.85 8.82	68.61 8.63

The following Table illustrates the copolymerization of representative antioxidant monomers with styrene. In this copolymerization, the antioxidant monomer and styrene are dissolved in twice the amount of benzene (using the first two antioxidant monomers in the Table below) or chloroform (using the last two antioxidant monomers set out in the Table below). The polymerization is conducted in the presence of 2% by weight of the monomers of 2,2'-azo-bis-isobutyronitrile and at a temperature of 80°C for 16 hours, under nitrogen. Following this, the polymer solution is diluted with chloroform to a 10% by weight solution and precipitated into 20 times the amount of methanol. The precipitated polymer is filtered and high vacuum dried. Yields vary between 91% and 95% by weight. All polymers are white, brittle powders.

TABLE VI

Copolymer Composition		Mol. Weight
Antioxidant Monomer (% by weight)	Styrene (% by weight)	(determined by osmometry)
3,5-di-tert-butyl-4-hydroxyphenyl crotonate 10.2	89.8	12,080
3,5-di-tert-butyl-4-hydroxyphenyl cinnamate 11.8	88.2	14,300
bis(3,5-di-tert-butyl-4-hydroxy-phenyl) fumarate 13.9	86.1	15,600
bis(3,5-di-tert-butyl-4-hydroxy-phenyl) itaconate 14.5	85.4	16,700

The oxidation of most polymers is so slow at ambient temperatures, even in the absence of antioxidants, that testing of the effects of antioxidants must be conducted at high temperatures to yield results within a convenient time. The tests conducted on the materials listed in the following Tables were conducted in a tubular oven with an air flow of 400 per minute at an oven temperature of 150°C. The oven aging is set out in hours. The expression "Failure" indicates the first sign of decomposition of the polymer.

In preparing the sample for testing, unstabilized polypropylene powder is thoroughly blended with the indicated polymeric antioxidant. The blended material is thereafter milled on a two roller mill at a temperature of 182°C for six minutes after which time the stabilized polypropylene is sheeted from the mill and allowed to cool. The milled polypropylene sheet which has been stabilized is then cut into small pieces and pressed for seven minutes on a hydraulic press at 218°C and 174 pounds per square inch pressure. The resultant sheet of 25 ml thickness is then tested for resistance to accelerated aging in the above described tubular oven.

TABLE VII

Oven Aging Tests of Polypropylene Films of 25 Mil Thickness Containing Different Polymeric and Oligomeric Antioxidants

Monomers	Polymers⑥ High-Mol.-Weight		Oligomers⑦ (Pentamers)	
	Hours To Fail:		Hours To Fail:	
	0.25% Anti-oxidant	0.1% Anti-oxidant + 0.3% DSTDP⑧	0.2% Anti-oxidant	0.1% Anti-oxidant + 0.3% DSTDP
3,5-di-tert-buty.-4-hydroxyphenyl methacrylate	<7	145	525	1075
2-(3,5-di-tert-butyl-4-hydroxybenzoyloxy)-ethyl methacrylate	<7	484	29	633
2-[3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionyloxy]ethyl methacrylate	29	120	790	1240
2-[3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionyloxy]propyl acrylate	<25	260	595	950
N-(3,5-di-tert-butyl-4-hydroxybenzyl)-acrylamide	<18	270	140	260

Where no antioxidant is added to the polypropylene in the above oven aging test, the "Hours to Fail" is less than 5 hours.

⑥ The synthesis of the high molecular polymers is described in Table III supra.

⑦ The antioxidant monomers listed in the Table above and n-dodecyl mercaptan in a molar ratio of 5:1 and 1% by weight of 2,2'-azo-bis-isobutyronitrile (based on the monomer) are dissolved in double the amount of chloroform and sealed under nitrogen. After polymerizing for 16 hours at 80°C, the solvent is evaporated and the oligomeric antioxidant is high vacuum dried. The yield is quantitative, that is about 100%, in all of the examples.

⑧ Distearylthiodipropionate.

The results of oven aging test of polypropylene films of 25 ml thickness, containing oligomers of 2-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy]ethyl methacrylate prepared with different mercaptans, is set out below in Table VIII. The procedure used involved dissolving a mixture of the aforesaid monomer and the mercaptan (mixed in molar ratios as indicated in Table VIII) and 1% by weight of 2,2'-azo-bis-isobutyronitrile (based on the monomer), in three times the amount of benzene and sealing under nitrogen. After polymerizing for 16 hours at 70°C, the solvent is evaporated and the oligomeric antioxidant is dried under high vacuum. The yields are in all cases quantitative, that is 100%.

TABLE VIII

Mercaptan (moles/per mol monomer)	Appearance of Oligomer	Hours to Fail: 0.25% Anti-oxidant	Hours to Fail: 0.1% Anti-oxidant + 0.3% DSTDP
n-octyl mercaptan (0.4)	high viscous polymer	970	1435
n-octyl mercaptan (0.2)	white, slightly tacky polymer	800	1325
n-dodecyl mercaptan (0.4)	high viscous oil	845	1315
n-dodecyl mercaptan (0.2)	white, slightly tacky polymer	790	1240
n-hexadecyl mercaptan (0.4)	high viscous oil	1040	1215
n-hexadecyl mercaptan (0.2)	white, tacky polymer	725	1225

Where no antioxidant is added to the polypropylene in the above oven aging test, the "Hours to Fail" is less than 5 hours.

In Table IX below, there are set out the results of oven aging tests conducted using copolymers of 2-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxy]ethyl methacrylate and different comonomers. The copolymers set out in this Table are prepared using the procedure set out in Table VIII above (n-dodecyl mercaptan, 0.2) except for the fact that 50% by weight of the monomer is replaced by the comonomers set out in Table IX below.

TABLE IX

Comonomer (50% By Weight of Copolymer)	Appearance of Oligomer	Hours to Fail 0.25% Anti-oxidant	Hours to Fail 0.1% Anti-oxidant and 0.3% DSTDP
None	colorless, high viscous oil	845	1315
methyl methacrylate	colorless, tacky polymer	450	435
n-octyl methacrylate	colorless, high viscous oil	850	949
n-dodecyl methacrylate	colorless, high viscous oil	1040	1075
n-octadecyl methacrylate	colorless, high viscous oil	995	1020
styrene	colorless, high viscous oil	430	830
1-vinylnaphthalene	light yellow, high viscous oil	83	558
N-vinyl carbazole	milky tacky polymer	800	875

Generally, the oligomers, even after oven failure, showed only little change in color. However, where no antioxidant was added the "Hours to Fail" was less than 5 hours.

In Table X set out below, the results of tests are set out in oligomers of 3,5-di-tert-butyl-4-hydroxyphenyl methacrylate and n-dodecyl mercaptan. The polymerization was effected by dissolving a mixture of the aforesaid monomer and n-dodecyl mercaptan (in molar ratios as set out in the Table), and 1% by weight based on monomers of 2,2'-azo-bis-isobutyronitrile in twice the amount of chloroform. After sealing under nitrogen and polymerizing for 16 hours at 70°C, the solvent is evaporated and the oligomer is dried under high vacuum. The yields are quantitative.

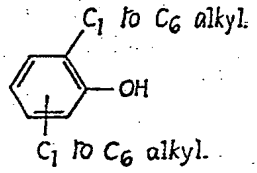
TABLE X

Ratio (molar) Mercaptan / Monomer	MW of Anti-oxidant	Appearance of Oligomer	Hours to Fail: 0.25% Anti-oxidant	Hours to Fail: 0.1% Anti-oxidant and 0.3% DSTDP
1/2	783	white, high viscous oil	930	1270
1/2.5	925	white, tacky polymer	940	1600
1/3.3	1165	white, solid polymer	800	1415
1/5	1654	white, brittle polymer	525	1075
1/10	3106	white, brittle polymer	330	490

It was noted that there was no discoloration even after oven failure. Where no antioxidant is used, the "Hours to Fail" was less than 5 hours.

WHAT WE CLAIM IS:—

1. A process for the preparation of a polymeric antioxidant compound, which process comprises subjecting to polymerising conditions (a) a monomeric ester, thioester, amide or imide of an α,β-ethylenically unsaturated carboxylic acid containing in the moiety attached to the α,β-ethylenically unsaturated carboxylic acyl moiety a phenol group of the formula:



and (b) a free radical initiator which is an azo derivative, or an aliphatic or cycloaliphatic acyl peroxide.

2. A process according to claim 1 wherein the monomer used is selected from esters, thioesters and amides of acrylic and methacrylic acid; esters, thioesters and amides of maleic acid, fumaric acid, citraconic acid and mesaconic acid; imides of maleic acid and citraconic acid; esters, thioesters and amides of itaconic acid; and esters, thioesters and amides of crotonic acid and cinnamic acid.

3. A process according to claim 1 or 2 wherein the initiator (b) is an azo nitrile.

4. A process according to claim 3 wherein the azo nitrile is 2,2'-azo-bis-isobutyronitrile.

5. A process according to claim 1 or 2, wherein the initiator (b) is an aliphatic or cycloaliphatic acyl peroxide having up to 18 carbon atoms in each acyl group.

6. A process according to claim 5 where the peroxide is acetyl peroxide, lauroyl peroxide or decanoyl peroxide.

7. A process according to any of claims 1—6 wherein a comonomer compound is included in the polymerisation reaction.

8. A process according to claim 7, wherein the comonomer compound is selected from C_1—C_{24} alkyl acrylates and methacrylates, styrenes, vinyl esters, butadiene and isoprene and chlorinated and fluorinated derivatives thereof, and the said monomer (a) is an acrylate or methacrylate.

9. A process according to claim 1 wherein the polymerization is carried out in the presence of a chain transfer agent.

10. A process for the preparation of polymeric antioxidant compounds substantially as hereinbefore described with reference to the foregoing Tables II to X.

11. Polymeric antioxidant compounds whenever prepared by a process as claimed in any of claims 1 to 10.

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